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The Action of Polar Organic Inhibitors in the Acid Dissolution of Metals

by

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The Action of Polar Organic Inhibitors in the Acid Dissolution of Metals

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Abstract

The theory of cathodic inhibition by polar organic compounds principally
developed by Mann and his co-workers is critically examined and found
inadequate to account for experimental results reported in the literature
Modifications of this theory are also not in agreement with experiment,
particularly with the shift in the cathodic direction of the open circuit
potential generally observed upon addition of inhibitors.   General
adsorption theories, on the other hand, are not in conflict with reported
results but a specific mechanism for inhibition is lacking.

A mechanism for inhibition by polar organic compounds based on recent
advances in the field of chemisorption on metals is presented. Inhibition
is considered to be the result of both physical adsorption and chemisorption.
Electrostatic bonding at cathodic areas contributes to over-all inhibition
However, polarization of anodic dissolution because of chemisorption of
inhibitor is more pronounced than cathodic polarization   Inhibitor
chemisorption occurs through coordinate covalent bond formation with
surface atoms of the metal.   The inhibitor acts as donor and the metal
as acceptor.

Dependence of inhibitive power on electronic structure of the functional
group, on solubility, and on substituents on the inhibitor is satisfactorily
explained by this mechanism   The theory allows for different metals
and permits both positive and negative temperature coefficients. Stereo-
chemical effects occur but are of less importance than previously thought
Results reported in the literature for nitrogen- and sulfur-containing
compounds, aldehydes, and ketones are shown to be in agreement with
this mechanism   The effect of an ethylenic linkage in the inhibitor and
the "ortho effect" are also consistent with this mechanism.

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The three prerequisites of an electrochemical mechanism of corrosion
are (i) a potential difference, (ii) a conduction path, and (iii) availability
of electrode reactions for transferring charges across the metal-solution
interface (14, 22).   Thus, an inhibitor may function: (a) by increasing
the true ohmic resistance and (b) by interfering with either the anodic,
the cathodic, or both the electrochemical processes.   Examples of case

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(a) are inhibition by the formation of an oxide film or by precipitation of
a non-conducting reaction product onto the metal. Inhibition caused by
an increase in the activation hydrogen overpotential, or by a decrease
of potential differences on the metal surface, or by activation polarization
of anodic dissolution are examples of case (b).

Theories of Cathodic Inhibition

A theory for the action of organic inhibitors was suggested by Chappell,
Roetheli, and McCarthy (5) who studied the effect of quinoline ethiodide
on cathodic and anodic polarization of iron and steel in N H_2SO_4 and
concluded that inhibition was cathodic. The same conclusion was
reached by Mann who proposed a comprehensive theory of inhibition by
organic compounds (33). Essential features of this theory (6, 31, 32, 33)
are that organic inhibitors are capable of forming onium ions and
accordingly exist in acid solution as cations. These are cathodically
adsorbed by virtue of electrostatic attraction and thus blanket cathodic
areas The resultant film increases the interfacial resistance to passage
of current by preventing hydrogen ions from reaching the surface, the
nature of the cathode not being actually changed. Depending on extent
of adsorption, the closeness of packing in the adsorbed film, and cross
sectional area of the molecule, various degrees of inhibition obtain.
Thus, according to Mann, organic inhibitors operate by mechanism (a).

Evidence for this theory comes from cathodic polarization studies and
from changes of the inhibitive power caused by substitution on the
inhibitor. Results of measurements of film resistance (2, 30, 40) are
conflicting and difficult to interpret theoretically. Machu (30) found a
direct relationship between film resistance and inhibition. Bockris and
Conway (2), however, found a negligible film resistance and concluded
that Machu's explanation of inhibition as a resistance effect was highly
improbable.

A number of polarization studies have been reported (2, 5, 13, 28, 34,
38, 43) In general, the major effect of inhibitors at the current densities
employed was on cathodic polarization. At high current densities and
very negative potentials, as used in such studies, the effect of inhibitors
on the cathodic reaction undoubtedly becomes greater. However, these
conditions are quite removed from those existing during corrosion (open
circuit) and any conclusion drawn from such studies are liable to be
erroneous (25).

Mann's theory enjoyed a wide following mainly because it conformed to
the inherent notion that positively charged particles should be adsorbed
only on negatively charged areas. There are, nonetheless, numerous

difficulties barring its acceptance   One major difficulty is presented by
the change of the open circuit potential in the cathodic direction generally
observed on addition of inhibitors.   This shift can be explained easily if
one assumes that the main effect of the inhibitor is on the anodic reac-
tion (26)   To account for this potential change on the basis of Mann's
theory, or any modification of it, the assumption must be made that the
organic compound is either reducible or can depolarize the cathode (13)
It is difficult, however, to see how a compound at some fixed concentration
can be both a depolarizer and an inhibitor of the same process simulta-
neously.   Further, many inhibitors which give such shifts, e.g , the
amines (21, 26), are incapable of undergoing cathodic reduction under
conditions existing in corrosion

A second major difficulty is that both anodic and cathodic effects occur
in polarization studies at small current densities   Cavallaro and
Bolognesi (3) found by polarization methods that a number of inhibitors
were of a mixed type and in many cases prevalently anodic.   Hackerman
and Sudbury (21) report both anodic and cathodic effects in polarization
studies with n-octyl amine.   Kuznetsov and Iofa (29) also report that in
many cases the increase in overpotential caused by inhibitors is greater
on anodic polarization (29).

A third difficulty arises from specific effects observed with inhibitors.
Sulfur-containing compounds are better inhibitors than corresponding
nitrogen compounds.   The theory of cathodic inhibition makes no provision
for such effects since electrostatic forces are not specific.   If there is
any difference in the extent to which an amine or a thiol exist as cations
in acid solution, the amine ought to exist to a greater extent as the cation
since it is the more basic.   Hackerman and Cook (20) found that irrevers-
ible adsorption of acids, alcohols, and esters occurred on the same portion
of a steel surface while amines adsorbed irreversibly on a different
portion   This is another instance of specific adsorption which indicates
that other forces besides electrostatic ones are operative.

A similar difficulty is encountered when it is necessary to account for the
effect of the nature of the metal   Thiourea is a good inhibitor for
aluminum, whereas it has no effect on zinc and accelerates the dissolution
of cadmium (27)   Potassium cyanide is an inhibitor for aluminum and
zinc but has no effect on cadmium; KCNS stimulates corrosion of cadmium
and zinc by HCl but retards that of aluminum and iron (3).   Also, organic
inhibitors are in general poorer for zinc than for iron

The theory of cathodic inhibition requires that the temperature coefficient
for inhibition be negative, whereas experimentally (21, 28) both positive
and negative temperature coefficients are reported.

As the number of substituents on the functional group of an inhibitor
increases, the inhibitive power in general also increases Mann attributes
this to a more complete coverage of cathodes because of increased cross
sectional area and increased adsorption (6, 33)   Swearingen and Schram(42),
however, report that a series of amines of approximately equal cross
sectional area exhibit quite different inhibitive properties   Fron: this
they conclude that specific adsorption is important in inhibition. Cardwell
and Eilers (4) also found a specific effect upon introduction of a methyl
group in the ortho position of various heterocyclic nitrogen compounds
used as inhibitors   Cavallaro and Bolognesi (3) have shown that high
molecular weight is not necessary for good inhibition if a strongly sorbing
group is present in the molecule   The degree of inhibition exhibited by
small molecules is also unexpected on the basis of this theory.   For
example, KCNS shows 65 per cent inhibition (3) as compared to 55 per
cent by n-butyl amine and 65 per cent by n-amyl amine (33).

The suggestion that all substances employed as inhibitors exist in acid
solution as charged ions has been questioned (26, 30)   Hoar (26) points
out that o-tolyl thiourea probably, and sulfonated castor oil certainly,
are neutral molecules in 10 per cent H_2SO_4 but nevertheless, are ex-
cellent inhibitors   To these can be added methyl sulfide, butyl disulfide,
and other sulfur compounds   Hoar further considers that electrolytic
migration of a large positive ion in a solution containing a great excess
of H_3O^+ would be negligible   He also points out that cathodes on the
surface are polarized by the corrosion current to a potential "which is
probably well within a millivolt" of that of anodes and therefore "the
absolute potential difference between the bulk of the metal and the bulk
of the solution is substantially uniform over the entire surface so that
no specific (cathodic) adsorption can be expected".   Finally, Hackerman
and Schmidt (19) point out that compounds giving negatively charged ions
in solution function as inhibitors.

Some of the above objections can be met by a modification of Mann's
theory which retains the basic concept of the theory, viz. cathodic
adsorption, but ascribes inhibition to an increase of the hydrogen activation
overpotential.   This theory, favored by Bockris and Conway (2), and
Elze and Fischer (13) among others, can account for the specific effects
by inhibitors but not for the shift in the cathodic direction of the open
circuit potential unless the previous unsatisfactory assumptions are
made

Inhibition and General Adsoprtion

The difficulties encountered by Mann's theory have led to consideration
of inhibition as the result of general rather than cathodic adsorption.
Machu (30) attributed inhibition to increased ohmic resistance resulting
from physical adsorption over the entire surface. Fink (16, 17) also
proposed that general adsoprtion of the inhibitor occurred. According
to him, however, this adsorption is "chemical" in nature and leads to
polarization of both anodes and cathodes, with consequent surface
"equipotential ation" and diminished corrosion. This thesis is substan-
tially the same as that of Hackerman and Sudbury (21) and Hackerman
and Schmidt (19). The theory of general adsorption is also favored by
Hoar (26). A mechanism, however, that would count for the observed
facts is still lacking and the nature of the adsorption forces is not clear.

Considerable progress has been made in recent years in elucidating
various types of bonds formed in adsorption, particularly in connection
with studies in heterogeneous catalysis (8, 9, 12). Of special interest
here is the work of Maxted (35, 36) who observed that compounds con-
taining elements of groups Vb and VIb of the periodic table were
particularly effective as poisons of platinum and nickel catalysts. A
common characteristic of these elements is the presence of a pair of
electrons that can be donated in coordinate covalent bond formation.
That the toxic character was a function of this pair of electrons was
shown by the absence of toxicity in compounds where these electrons
were shielded. Corroborating evidence was provided by the observation
that substances which contain unsaturated bonds, such as ethylene,
carbon monoxide, and cyanogen compounds, are also strong poisons.

Catalytic poisoning results from strong adsorption of a substance (the
poison) which ties up active sites of the catalyst that could otherwise
be utilized in the catalytic process. Thus, a poison operates by being
strongly chemisorbed on the metal catalyst. Maxted, therefore, concluded
that chemisorption of these compounds on metallic hydrogenation catalysts
of group VIII was accomplished through a dative link, the metal func-
tioning as acceptor and the sorbate as donor. In addition, he postulated
that the electron pair was donated to the d-shell of the metal This last
assumption received experimental support from magnetic susceptibility
measurements (7).

Polar organic compounds containing elements of groups Vb or VIb are
effective as inhibitors in the acid dissolution of metals Some partic-
ularly effective functional groups are -CN, -CNS, -CNO, $>$CO, and -CHO.
These compounds are "electron rich" and can act as electron donors.
It will be shown that a satisfactory explanation of inhibitive action of

these compounds can be found along lines suggested by Maxted in his work on catalytic poisoning. The two systems are similar in that adsorption is the primary step in both cases.

Adsorption of Polar Organic Inhibitors

It is postulated that adsorption is general and not decisively controlled by the existence of local cells. The improbability of any considerable electrolytic migration of inhibitors during corrosion was shown above.

This adsorption is both physical and chemical in nature. Physical adsorption results from weak van der Waals, or dispersion, forces which are operative over the entire surface. In addition adsorption because of electrostatic interaction occurs at cathodes. The amount adsorbed because of dispersion forces, though not negligible, is of little importance in inhibition by compounds discussed here. This, of course, does not apply to substances like gelatin which are barrier-type or diffusion inhibitors. Electrostatic bonding at cathodic areas contributes, however, to over-all inhibition*.

It is postulated that considerable chemisorption occurs under the conditions existing in acid dissolution. The studies of Hackerman and Cook (20) on adsorption of inhibitors from benzene solution on steel powder constitute the experimental basis for this postulate. Additional experimental support is provided by the persistence of inhibition when pretreated iron coupons are transferred from protected solutions to unprotected ones (3, 31).

The binding responsible for chemisorption is the formation of a dative link between the metal and the organic molecule. The bond is formed through sharing a pair of electrons from the inhibitor with the metal. Since such a transfer leaves the organic molecule with a formal positive charge, it is unlikely that more than one electron pair per molecule will be donated even though the acceptor might have available orbitals for more

It should be noted that chemisorptive bonds can also be formed where the metal acts as donor and the adsorbate as acceptor Such a mechanism is probably responsible for inhibition by various metal ions. It is,

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*Since most of these inhibitors exist as positively charged ions in solution, the adsorption resulting from electrostatic forces is cathodic. In the case of inhibitors yielding anions in solution, such adsorption will occur at anodes.

however, doubtful that any organic inhibitors are chemisorbed in this fashion

Chemisorption might cause inhibition either by decreasing the dissolution tendency of the metal at anodes, or by increasing the activation over-potential for hydrogen discharge, i.e , by poisoning the cathodes. It should be emphasized that either of these requires that the inhibitor be chemisorbed: physical adsorption involves energies which are not of the right order of magnitude for such effects.

No a priori reason can be given as to why the effect of chemisorbed inhibitor should be greater on anodes rather than on cathodes. The requirements for anodic and cathodic inhibition are the same, viz. chemisorption of the inhibitor, though the result of such chemisorption is different in the two cases At anodes the inherent reactivity of the metal is decreased whereas at cathodic points the hydrogen reaction is poisoned It is impossible to decide between the two on theoretical grounds since neither of these phenomena is well understood Experiment, however, indicates that the inhibitive action is prevalently anodic Largely, the experimental evidence comes from the cathodic shift of the open circuit potential on addition of inhibitors This requires that polarization of the anodic reaction be more pronounced than polarization of cathodic hydrogen deposition

Anodic polarization may be looked upon as the result of chemisorption with consequent stabilization of the metal ion in the surface lattice Alternatively, it may be described as complex formation in situ, many inhibitors are capable of forming complexes with ferrous ion, and on the basis of this property only they should be accelerators rather than inhibitors A similar situation exists with amines and copper In these cases complex ion formation in situ offsets the accelerating effect of complexing the metal ion in solution so that over-all inhibition rather than acceleration results

A third way of looking at anodic polarization is to follow Evans and Hoar(15) and consider it as the arrest of emergent cations, a description which permits a smooth transition from oxidation studies at high temperature to wet corrosion All of these descriptions are equivalent The first viewpoint is used here because it proves to be not only the most convenient but also the most fruitful

Inhibition, then results from both increased resistance to current flow caused by electrostatic adsorption at cathodic areas and from anodic polarization caused by chemisorption The relative contribution of the two depends on the inhibitor Three classes of inhibitors may thus be distinguished Anodic inhibitors function by polarizing anodic dissolution

An example is the sulfide series   A second class consists of mixed inhibitors   Examples are amines and thiols   Finally, there are cases where cathodic polarization is the most important effect   Quaternary amine salts belong to this class   Here, although physical adsorption probably occurs over the entire surface, chemisorption does not take place since there is no possiblity of electron transfer.   The strongest possible bonding with R_4N^+ is electrostatic attraction and this obtains at cathodes

Factors that critically influence the extent of chemisorption are the nature of the metal and the electronic structure of the adsorbed group   The strength of bonding is a function of the metal since it is related to residual valence orbitals existing at the metal surface   Without going into various treatments of chemisorption it may be noted that residual metal valencies at the surface are not alone sufficient for strong chemisorption, in addition, unfilled atomic orbitals are required   Pauling's treatment of the metallic state would apply here   These are principally of d character   Inhibitors of this type should, therefore, be more effective, for example, with iron than with zinc

An elementary approach to the influence of the electronic structure of the adsorbed group is possible in terms of the availability of electrons for bond formation   This can be considered to be a function of electron density and polarizability of the functional group or, for simple molecules, of the Vb or VIb element that the compound contains   This is admittedly an approximation, but the complexity of the system here considered does not permit a more rigorous treatment

Applications of the Mechanism

Taking iron as the metal to be protected, consider the action of polar organic inhibitors in the light of the above postulates   The data of Mann (31, 32, 33) and other results obtained at the University of Minnesota by Mann and his co-workers and tabulated by Eldredge and Warner (11) are used

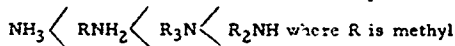Amines: Inhibition by aliphatic amines considered to involve the following equilibria:

$$RNH_3^+ \text{ (sol.)} \rightleftharpoons RNH_2 + H^+ \rightleftharpoons RNH_2 - \text{Iron}$$
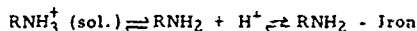
where RNH_2 - Iron denotes chemisorbed amine   The extent of chemisorption depends on the strength of the amine-metal bond and also on the solubility of the particular amine   This last factor should be particularly
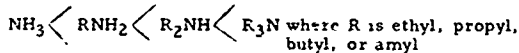
noted in view of some definitions of chemisorption as "irreversible adsorption" Chemisorption, like any other chemical reaction, is more or less easily reversible depending on the specific system under consideration Maxted (37) has shown that catalytic poisons, which are undoubtedly chemisorbed, can be removed from a platinum catalyst simply by washing with fresh solvent. The extent of chemisorption is thus a function of the solubility of the chemisorbed compound and consequently, inhibition is also a function of solubility.

The strength of the iron-amine bond is a function of both electron density on the nitrogen atom and the availability of these electrons for coordinate bond formation The basic strength of the amine is taken to be an indication of the electron density on the nitrogen atom, and the assumption is made that the strength of the chemisorption bond increases with increasing basic strength. This criterion alone is of limited usefulness since the availability of electrons for coordination is also a function of the polarizability of the atom or group considered. However, in the absence of any other information, this criterion must be used

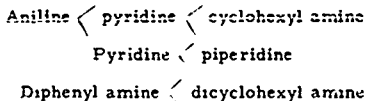The relative order of inhibitive effectiveness of aliphatic amines is

$$NH_3 < RNH_2 < R_3N < R_2NH \text{ where R is methyl}$$

and

$$NH_3 < RNH_2 < R_2NH < R_3N \text{ where R is ethyl, propyl, butyl, or amyl}$$

In the first series basic strength decreases in the order R_2NH, RNH_2 $R_3N > NH_3$ (24) The solubility of the methylamine salts is about the same. Thus dimethyl amine is a stronger base and approximately as soluble as trimethyl amine. Dimethyl amine should thus be a better inhibitor than trimethyl amine. For the second series, however, the decrease in basicity of diethyl amine upon introduction of a third ethyl radical is significantly less (about one-fourth as much)(24), and triethyl amine is less soluble than diethyl amine (41). Consequently, triethyl amine should be more effective than diethyl amine This is true also where R is propyl, butyl, or amyl

The introduction of a fourth alkyl group causes a sharp drop in inhibitive power Thus, both trimethyl and dimethyl amines are better inhibitors than tetramethyl ammonium ion Such decrease in inhibition is understandable on the basis of this theory since chemisorption of the quaternary salt cannot occur. Inhibition by this ion is, therefore, for the main part cathodic

Aliphatic amines are better inhibitors than aromatic amines. Hetero-
cyclic amines, such as pyridine, while better than aromatic amines are
less effective than the corresponding saturated compounds. These
relations are shown schematically below:

$$Aniline < pyridine < cyclohexyl\ amine$$

$$Pyridine < piperidine$$

$$Diphenyl\ amine < dicyclohexyl\ amine$$

The basic strength of these compounds is in the same order (24). A
phenyl group is electron attracting and it consequently decreases the
electron density on the nitrogen atom, the decrease being reflected in
lower basic strength of aniline when compared to cyclohexyl amine.
Piperidine is also a stronger base than pyridine. Saturation of the
aromatic or heterocyclic ring increases electron density on the nitrogen
atom and therefore increases inhibitive power (6).

Data for benzyl amine are not available   The theory requires that its
inhibitive power lie between that of aniline and cyclohexyl amine

The introduction of alkyl groups on the benzene ring of aniline leads to
better inhibition because of both decreased solubility and increased
electron density on the nitrogen atom.   The same is true when hydrogen
atoms on nitrogen are replaced by alkyl groups   Relations that result
are similar to those for aliphatic amines

Steric effects are operative but are of less importance than previously
thought(33)   Further, such effects are not restricted to cathodic adsorption
but influence adsorption in general as shown by studies on charcoal(44)
On the basis of this theory geometrical factors should determine the
closeness of packing of the adsorbed film over both anodes and cathodes
and consequently affect the inhibitive power   Thus, the decrease in
inhibition generally observed on substitution of a branched alkyl chain
for a straight one is caused by the methyl group in iso compounds
preventing close contact of neighboring adsorbed molecules.   As a result,
not only is adsorption decreased but also effectiveness of the film over
both anodes and cathodes reduced

The stereochemical configuration of inhibitors might also influence the
extent of adsorption through its effect on the degree of association of
polar organic compounds in solution.   The monomeric form is known
to be preferentially adsorbed and, therefore, any change in the degree of
association will undoubtedly be reflected on extent of adsorption

The Ortho Effect: Introduction of methyl groups on the ring of pyridine and other heterocyclic aromatic nitrogen compounds increases inhibition just as in the case of aniline and for the same reasons   Cardwell and Eilers (4) observed that a methyl group in the ortho position was particularly effective; and that it caused a constant 25 per cent increase in inhibition, independent of the original cross sectional area of the inhibitor Rhodes and Kuhn (40) report that in the series pyridine-lutidene-picoline-collidine the introduction of a methyl group increases inhibition by about 25 per cent   Mann (11) also found that the effectiveness of toluidines is in the order

<p style="text-align:center">aniline $<$ m-toluidine $<$ p-toluidine $<$ o-toluidine.</p>
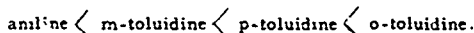
The main effect of the methyl group is on the strength of the chemisorption bond and, qualitatively, is due to its ability to supply electrons to the ring.   Taking aniline as an example, the following resonance states contribute to the over-all structure:
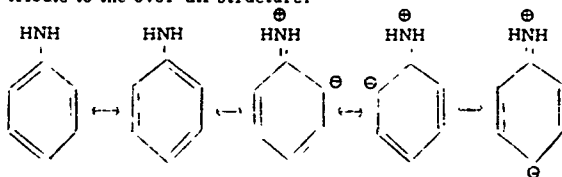
Substitution of electron donating methyl groups decreases the contribution of the last three structures and thus leads .o increased chemisorption. From these structures it seems reasonable that, other things being equal, substitution in the ortho or para positions should be more beneficial than substitution in the meta position.   Similarly, in the case of pyridine an ortho group increases electron density on the nitrogen atom because of resonance, viz.
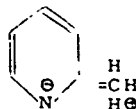
This is also true for a para methyl group but not for one in the meta position.

The specific effect by an ortho methyl group on the adsorption bond observed by Cardwell and Eilers (4) is thus in accord with this theory

Sulfur-Containing Compounds: The protective value of sulfur-containing compounds is decidedly superior to that of nitrogen containing compounds This is in part caused by the lower solubility of sulfu. compounds. However, even making allowances for this, sulfur compouncs are still found to be better inhibitors Ethyl mercaptar for example, is as good, if not better, an inhibitor as diamyl amine, dihexyl amine, or tripropyl amine

Superiority of sulfur compounds results from the greater polarizability of the sulfur atom Sulfur is less electronegative than nitrogen (2 5 compared to 3 0 on Pauling's scale) Furthermore, it has two electron pairs available for coordination whereas nitrogen has only one. Consequently, sulfur is a better electron donor than nitrogen, a property which is reflected in its greater tendency towards coordination. For this reason sulfur compounds are more extensively and more strongly chemisorbed than the "corresponding" nitrogen compounds The inhibitive power of compounds like methyl sulfide which is entirely unexpected on the basis of cathodic inhibition becomes understandable on the basis of this theory.

Within a series of sulfur compounds the same relations obtain as within the equivalent series of nitrogen compounds. Thus the order of effectiveness of mercaptans is

$$\text{methyl} < \text{ethyl} < \text{propyl} < \text{butyl} < \text{amyl}$$

and of sulfides

$$\text{methyl} < \text{ethyl} < \text{propyl} < \text{butyl}$$

A drop in inhibitive effectiveness is again observed in going from aliphatic to aromatic compounds Thus, thiophenol is poorer than ethyl mercaptan (data on cyclohexyl mercaptan are not available). The reason is the same as in the nitrogen compounds. As would be predicted on the basis of electron density, thiocresols are better than thiophenol.

Corresponding oxygen compounds, e.g , alcohols and phenol, are poor inhibitors. This is because oxygen is more electronegative than sulfur, and it does not readily function as a donor in coordinate bond formation Selenium, on the other hand, should give compounds that are better inhibitors than corresponding sulfur compounds. Data are available only for ethyl selenide. Judging from this alone, selenium is more effective than sulfur

Aldehydes and Ketones: In aldehydes and ketones the electronic con-
figuration of the functional group as a whole rather than that of any
particular atom is of importance, and a discussion of their inhibitive
action is consequently more involved   The inhibitive action of these
compounds is a function of the reactivity of the functional group
Aldehydes, which are more reactive, are better inhibitors than ketones
The inhibitive efficiency in the series RCHO, where R is H, CH_3, C_2H_5,
or C_3H_7, does not follow the pattern for amines or thiols but is in the
order:

butyraldehyde $<$ acetaldehyde $<$ propionaldehyde $<$ formaldehyde.

This relative order for inhibition indicates that two opposing effects
are operative as molecular weight increases, viz adsorption tends to
increase but reactivity decreases.

Substitution of a methyl group on the benzene ring of benzaldehyde causes
an increase in inhibitive power just as for nitrogen- and sulfur-containing
compounds.   Further meaningful comparisons cannot be made because
experimental data on aldehydes are much less available than for either
nitrogen or sulfur compounds   This is also true for ketones

The Effect of the Double Bond: Cavallaro and Bolognesi (3) observed
that an ethylenic double bond has considerable inhibitive power   For
example, where propyl alcohol is of very little inhibitive value, allyl
alcohol is a very good inhibitor   Similarly, they found that under con-
ditions where thiourea is an accelerator, allyl thiourea is a good inhibitor*
Mann (11) also found that crotonaldehyde is a much better inhibitor than
butyraldehyde and phorone is superior to valerone

Chemisorption of ethylenic compounds on metal catalysts is known to
occur   The superiority of unsaturated compounds is the result of
enhanced chemisorption brought about by the double bond, which con-
stitutes a second point of attachment of the inhibitor   In conjugated
systems the electron density of the aldehyde, or keto, or other
functional group is augmented by the resonance that results, and this
also contributes to stronger chemisorption

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*The data reported in the literature concerning the inhibitive actions
of thiourea and its N-substituted derivatives are conflicting.   This
is because these compounds function in more than one way depending
on conditions   Reference (23) is an attempt to clear up the conflicting
reports on the basis of a study of eight of these compounds under
various conditions

Other Inhibitors: For inhibitors having other functional groups there is insufficient information for significant comparisons. An interesting observation is that substitution of sulfur for oxygen leads to better inhibitors as is expected Thus, thioureas are better inhibitors than ureas and thiocanates, better than cyanates.

Of the diverse list of inhibitors remaining to be considered, some are difficult to account for with the proposed mechanism. For example, according to this theory sulfates and sulfonate should not have inhibitive properties to any considerable extent Experimentally it is found that sulfates are not good inhibitors (4),(11), (and data obtained in this laboratory) Results reported on sulfonates are conflicting Eldredge(11) found two commercial wetting agents (both sulfonates) to be good inhibitors. Cardwell and Eilers (4), however, report no inhibition by a saturated hydrocarbon sulfonate. In order to account for the discrepancy it would be necessary to know about the purity of the compounds used. This suggests that further work with carefully purified materials is needed

The problem of high molecular weight inhibitors should be mentioned here When the carbon chain gets up to about twelve carbon atoms or more, influence of the functional group on inhibitive properties is less pronounced than with low molecular weight inhibitors. With high molecular weight inhibitors, a densely packed film, with the hydrocarbon chains oriented outward, is formed on the metal surface Such films are known to be both hydrophobic and oleophobic (1)(39). It is probable that in this case inhibition is caused by a mechanical separation of the two phases, i.e., by the establishment of a diffusion barrier to both Fe^{++} and H^+ The functional group here aids adsorption at the interface and contributes to formation of an oriented structure One way in which the functional groups of high molecular weight compounds cause differences is in the persistence of inhibition. The order of effectiveness of functional groups in this respect is similar to that for low molecular weight inhibitors Thus inhibition by amines, thiols, and acids is more persistent than by alcohols and esters (20)

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